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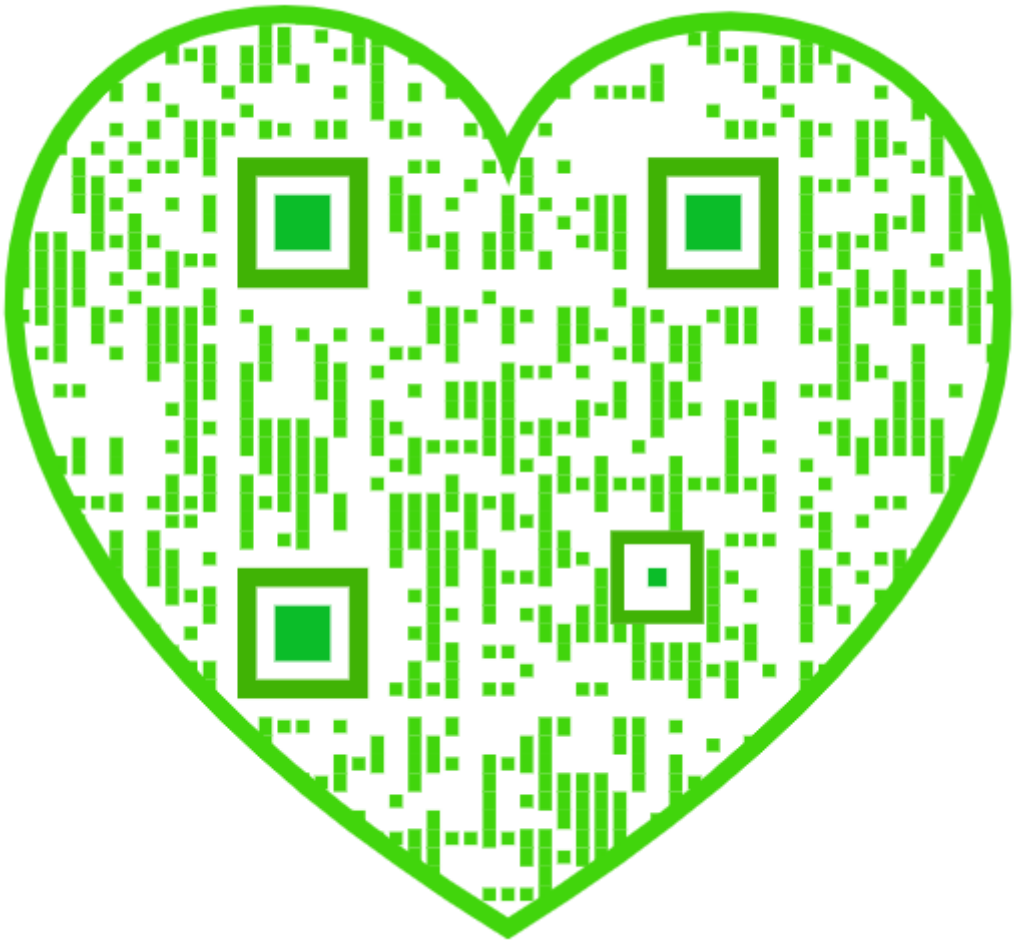
THE PREPARATION OF SUBSTANCES

CHARLES A. PETERS



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The Preparation of Substances Important in Agriculture

A Laboratory Manual of Synthetic Agricultural Chemistry

THIRD EDITION

BY

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PREFACE

It has been the aim in this manual to select substances of agricultural interest, adapt them to laboratory preparation, and explain their chemistry to the best of our present knowledge not overlooking their practical significance.

The work was at first nothing more than laboratory directions, but the interest of the student gradually required the addition of explanatory matter to such a degree that the emphasis on an accompanying text has been greatly reduced. The method of presentation aims to put a few major points before the student and extend the work on such points over so long a time that the student will absorb it. The author feels that when a student, in his earlier years in college, works interestedly for a whole exercise around one thing he grasps something while if a dozen important points pass in review during the time he is left in a maze and gets little but technical benefit. While, however, the student is busy on the one

major piece of work other minor points may be gatherd around it and are readily absorbd.

In this collection of agricultural material it is interesting to note the points that are brot home to the student as the work develops Among these are oxidation, neutralization, distillation, crystallizatıcn, saturation, chemical calculations, metathesis, mass action, double salts, equilibrium and colloids. By making a process necessary to the production of material the student must grasp it or fail in the experiment. Take the seemingly simple matter of saturation. It is but the work of a minute to explain what is meant by the process; the student will give an intelligent expression of the phenomenon in a second minute; however, when in the laboratory he is making a preparation from two others, the success of which depends upon the preparation of two saturated solutions, then, and not until then, does the student understand saturation.

Only about half of the students entering this college have had farm experience. It ıs difficult to interest a student in the preparation of superphosphate or Bordeaux mixture unless he knows something of its use, hence the amount of space given in the notes to the practical use of each substance. This does

not lessen the value of the material for chemical instruction but rather enhances it.

The work was designd for students in an agricultural college who have already had such a knowledge of chemistry as is acquired from a year's work in the high school. It is intended to be done in two or three hour laboratory periods, and furnishes sufficient material for one semester of such exercises. The arrangement of the work is such that a laboratory full of students can all be doing the same thing at the same time without extended waiting; procedures, such as crystallization and cooling, taking place in the interim between exercises. With us it is customary to score the preparation when completed, as one would butter or milk, allowing something for quality and something for quantity and to give credit for the exercise only upon completion of the preparation.

The author is endeted to Professor A. A. Blanchard of the Massachusetts Institute of Technology not only for the development of synthetic method of laboratory work for first year work in college, but also for the privilege to adapt three preparations from his book, Synthetic Inorganic Chemistry, for use in this manual. The three preparations are

Potassium Nitrate, Copper Sulfate and Lead Nitrate.

The appreciation of the author is also exprest to Dr. H. S. Adams of New Brunswick, N. J., who was associated with this work in its early stages, and to Professor Ernest Anderson of this laboratory who has given this course for several years. Valuable suggestions have come from both these men.

The first edition was printed privately in 1914; the second was again mimeographed in 1916; the third is herewith offerd to those laboratories that have used the manual since 1914 and to others that wish to experience the fascination of the synthetic method in agricultural chemistry.

A few simplified spellings have been used.

AMHERST, MASS.,
August 1, 1918.

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The Preparation of Substances Important in Agriculture

SUPERPHOSPHATE

Superphosphate is made from the natural rock phosphate, finely ground, and sulfuric acid, the phosphate being acted upon as shown in equation (1) which follows:

(1) $Ca_3P_2O_8 + 2H_2SO_4 \cdot aq = CaH_4P_2O_8 \cdot H_2O + 2CaSO_4 \cdot 2H_2O$.

Calcium dihydrogen phosphate

Calcium sulfate (gypsum)

Two-thirds of the calcium of the tricalcium phosphate are replaced by the hydrogen of the acid. Chamber sulfuric acid is used. It is necessary to calculate the actual amount of tricalcium phosphate in the material at hand, the amount of sulfuric acid to act on 200 grams of this material and the amount of water that must be added to the sulfuric acid to make it of the proper strength.

Calculations. — (*a*) Note the purity of the phosphate rock and calculate the number of grams (*a*) of the tricalcium phosphate in

200 grams of the material used. Record the amount.

(*b*) From the equation given above calculate the number of grams (*b*) of H_2SO_4 necessary to react with (*a*) grams of $Ca_3P_2O_8$. Note the number.

(*c*) Read the specific gravity of the chamber acid from the spindle floating in the acid on the side shelf. Refer to the table of specific gravity and read off the weight of the H_2SO_4 in 1 cc. of the chamber acid. Calculate the number of cubic centimeters of chamber acid (*c*) necessary to contain the (*b*) grams of H_2SO_4. Record the volum.

(*d*) The chamber acid is too strong to be used directly on the rock phosphate and must be diluted until it has the specific gravity 1.53. Calculate the number of cubic centimeters (*d*) of this acid necessary to contain (*b*) grams of sulfuric acid. This is the volum to which (*c*) cubic centimeters of chamber acid should be diluted before the rock phosphate is added to it. Record the number.

Tabulate the results of the four calculations as indicated below and have them verified by an instructor before proceding with the work.

(*a*) Weight of $Ca_3P_2O_8$ in 200 grams rock phosphate,.....grams.

(*b*) Weight of H_2SO_4 required for 200 grams rock phosphate,.. ..... grams.

(*c*) Volum of chamber acid required for 200 grams rock phosphate, ...cc.

(*d*) Volum to which the (*c*) cc. of chamber acid must be diluted, ...cc.

Procedure. — Measure out the volum (*c*) of chamber acid and pour it into (*d*–*c*) cubic centimeters of water in a porcelain dish. Weigh out 200 grams of the rock phosphate and stir it slowly into the acid. Let the mixture stay in the evaporating dish until the next exercise. The hydrofluoric acid fumes that arise are to be avoided.

Notebook; Test for Soluble Phosphates. — Shake a little of the superphosphate with water, filter the solution, add to the filtrate a solution of ammonium molybdate and warm the liquid gently in a test tube. If the yellow precipitate of ammonium phosphomolybdate does not form after a few seconds its appearance may be hastend by adding a gram or two of solid ammonium nitrate. The addition of ammonium hydroxid followd by nitric acid will accomplish the same result including the heating; when this is done the solution must be left acidic with nitric acid.

If some of the natural rock phosphate is

treated similarly it will be seen that only an inappreciable amount of phosphate dissolvs in water.

Test for Lime. — Dissolv some of the superphosphate in water and filter as before. To the clear filtrate add a solution of oxalic acid or ammonium oxalate. The white precipitate that forms is calcium oxalate which shows the presence of calcium compounds in solution.

NOTES

The Beaumé hydrometer is an instrument for determining density that has wide industrial use. It is, however, unscientific as it has

SULFURIC ACID. SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS

Degrees Bé.	Sp. gr.	1 cc. contains grams H_2SO_4.
50.0	1.53	0.957
50.6	1.54	0.977
51.2	1.55	0.996
52.8	1.56	1.015
52.4	1.57	1.035
53.0	1.58	1.054
53.6	1.59	1.075
54.1	1.60	1.096
54.7	1.61	1.118
55.2	1.62	1.139

two separate scales, one for liquids heavier than water and one for liquids lighter than water, the two having no relation. Further,

neither scale bears any relation to true specific gravity. See Thorp, Inorganic Chemical Preparations, p. 32.

The solubility of the natural rock phosphate, or floats, in a short time under most soil conditions, is so slight that it has become a common practise to "dissolv" it, that is, to convert it into the water-soluble acid phosphate having only one-third of the original amount of calcium. Under ordinary business conditions one-half of all the sulfuric acid made in this country is used in this process.

Tricalcium phosphate, whether as rock phosphate, bones or the mineral apatite, is always associated with fluorin and generally chlorin. In addition rock phosphate is generally associated with calcium and magnesium carbonates, and sometimes iron and aluminum phosphates so that the reactions which take place with the sulfuric acid are more complicated than that given at the beginning of this exercise. The following are the more important:

(2) $2Ca_3P_2O_8 \cdot Ca_2FPO_4 + 7H_2SO_4 \cdot aq = 3CaH_4P_2O_8 \cdot H_2O + 7CaSO_4 \cdot 2H_2O + 2HF.$

(3) $CaCO_3 + H_2SO_4 \cdot aq = CaSO_4 \cdot 2H_2O + CO_2.$

(4) $2AlPO_4 + 3H_2SO \cdot aq = 2H_3PO_4 + 2Al(SO_4)_3 \cdot 18H_2O.$

The fertilizer manufacturer must determin the exact amount of sulfuric acid to be used for each substance present in the ground rock. The student is not askt to do this. However, to insure the presence of sufficient acid to combine with all these substances, the calcium phosphate content of the floats as given to the student is increased 5 to 10 per cent.

The strength of sulfuric acid used will vary according to the source and composition of the natural rock. If large amounts of calcium compounds other than phosphate are present a more dilute acid is used so that there will be water enuf to hydrate the land plaster (calcium sulfate) formd in the reaction.

The calcium fluorid present reacts with the sulfuric acid producing the disagreeable poisonous hydrofluoric acid gas. Avoid breathing the fumes from the mixture.

Notice that after standing the mass crumbles easily in the hand. After storing several weeks, during which time the action of the sulfuric acid continues until the insoluble phosphates are reduced to a fraction of one per cent, the material is ground, if necessary, and put on the market or used as a "base," *i.e.*, one of the substances from which fertilizers are made.

There being several calcium compounds in the rock phosphate which all appear finally as hydrated calcium sulfate (gypsum) it is not strange that the resulting superphosphate is composed of 60–70 per cent of gypsum. From this it is easy to see why superphosphate contains only 14 to 16 per cent of phosphoric acid (P_2O_5).

The deposits of rock phosphate at present being extensivly workt are found in South Carolina, Florida and Tennessee. The largest and most newly discoverd deposits are in Idaho, Utah and Wyoming.

A good grade of ground rock carries 65 per cent of tricalcium phosphate and the material not infrequently runs over 80 per cent. Inferior rock containing a few per cent of phosphoric acid and mixt with carbonate of lime is abundant, but it is not economical to ship this any great distance or treat it with sulfuric acid.

The use of "raw rock" *vs.* "dissolvd rock" is a much discust question in agriculture. Thru the East, on light soils and for intensiv cultivation, the dissolvd rock is used exclusivly; for some of the heavy soils of the West raw rock is recommended in connection with decaying organic matter. According to Professor Hopkins of Illinois the raw rock in a heavy soil is converted to dissolvd rock

by acid in the soil, the steps in the process being first, the production of ammonium carbonate, $(NH_4)_2CO_3$, from the amino groups, $-NH_2$, in the plant; second, the oxidation of ammonia to nitrous acid by bacteria; third, the conversion of the raw rock to dissolvd rock by the action of the nitrous acid which may be represented by the equation,

$$Ca_3P_2O_8 + 4HNO_2 + H_2O = CaH_4P_2O_8 \cdot H_2O + 2Ca(NO_2)_2;$$

and fourth, the oxidation of the calcium nitrite, $Ca(NO_2)_2$, to calcium nitrate, $Ca(NO_3)_2$, by the action of bacteria. Both the acid phosphate and the calcium nitrate resulting from the action are available to the plants for food. Naturally the plants richest in amino groups, such as clovers and alfalfa, are most desirable to plow under with the raw rock. This action of the dissolving of raw rock by acid in the soil has been demonstrated by Professor Hopkins in the laboratory, but others deny that it actually takes place in the soil.

As a general conclusion it may be said that all the phosphorus of acid phosphate is immediately available to plants while only a small amount of the phosphorus in the raw rock is available during one growing

season; however, the phosphorus in raw rock continues to become available, year by year, until the total amount is drawn upon. For cultural purposes the important question is whether or not there is sufficient phosphorus available in one season for the crop in question; this, of course, depends upon many factors which cannot be gone into here.

Analysis of Rock Phosphate. — An analysis of Tennessee rock phosphate taken from the American Fertilizer Handbook for 1908 is here given:

	Per cent
Moisture (loss on drying)	0.87
Combined water and organic matter (loss on ignition)	1.53
Sand and insoluble matter	2.76
Ferric oxid, Fe_2O_3	2.40
Alumina, Al_2O_3	1.99
Lime, CaO	49.07
Magnesia, MgO	0.24
Carbon dioxid, CO_2	1.08
Fluorin, F	2.98
Sulfur trioxid, SO_3	1.03
Phosphoric acid, P_2O_5	35.62
	99.57

When these figures are put together in an attempt to show the substances that existed in the original rock the data shown under colum (*a*) is obtaind. The composition of another sample of rock phosphate is shown

in colum (*b*). It is noticeable that many of the constituents vary widely in quantity.

	(*a*)	(*b*)
	Per cent	Per cent
Moisture and organic matter	2.30	1.00
Phosphate of lime, $Ca_3P_2O_8$	77.76	55.00
Phosphates of iron and aluminium $FePO_4$, $AlPO_4$	.....	6.50
Carbonate of lime, $CaCO_3$	4.43	3.50
Carbonate of magnesia, $MgCO_3$	0.50	0.75
Fluorid of lime, CaF_2	6.11	2.25
Iron pyrites, FeS_2	0.77	.....
Iron oxid, Fe_2O_3	1.88	.....
Alumina, Al_2O	1.99	.....
Sand and silicious matter	2.76	28.00
	98.50	100.00

The natural sources of phosphorus are the mineral apatite, or phosphorite, which is an ingredient of nearly all soils. It has the same formula as the raw rock phosphate but is entirely different in appearance. Immense deposits of this mineral are localized in Quebec and Ontario, Canada.

QUESTIONS

(To be answerd in the notebook.)

1. What is the per cent of P_2O_5 in calcium dihydrogen phosphate?

2. Supposing equation (2) to represent all that happens when sulfuric acid acts upon rock phosphate, calculate the per cent of hydrated acid phosphate and the per cent of hydrated calcium sulfate in the mixture.

3. Again supposing equation (2) to represent what happens when superphosphate is made, what is the highest per cent of P_2O_5 it is possible to have in superphosphates?

4. What per cent of P_2O_5 is present in ordinary superphosphate? Name the substance represented by the symbol P_2O_5.

5. What per cent of tricalcium phosphate is found in natural phosphates?

6. Which would use the more sulfuric acid, a raw rock carrying 60 per cent tricalcium phosphate and 5 per cent calcium carbonate or a rock carrying 55 per cent tricalcium phosphate and 10 per cent calcium carbonate?

7. What gases escape during the action of the sulfuric acid on the rock phosphate? Which is poisonous?

8. What compounds are found in the raw rock? In the dissolvd rock? The student cannot give, for example, calcium oxide, CaO, or phosphorus pentoxid, P_2O_5, as compounds present in either the raw or dissolvd rock altho such compounds are well known and moreover are represented in the table of analysis. In the raw and dissolvd rocks the lime and the phosphoric acid are in combination and the student should give, as well as he can, the actual lime and phosphorus compounds that are present.

9. How could phosphoric acid be made by a process similar to that for making superphosphate?

10. How could the acid phosphate be made into a neutral salt? How would the solubility change?

11. Write a symbol for another acid calcium phosphate; name the compound.

12. How is the test made for soluble phosphate?

13. Describe the test for lime.

14. How many grams of actual sulfuric acid in a liter of dilute acid of a density of 51.5 Bé.?

15. Where are the phosphate deposits in this country?

16. Where should a plant for making superphosphate be located? Near the phosphate mines or near the farmer? Give reasons for the answer.

17. What is meant by the terms, "raw rock," "dissolvd rock"?

18. Where is the use of dissolvd rock recommended?

19. Is calcium sulfate soluble in water? (See text under calcium compounds.)

20. Write symbols for limestone; slaked lime; quicklime.

SULFATE OF AMMONIA

Sulfate of ammonia is made by distilling the ammonia from the gas liquor into sulfuric acid. The first problem is to find out, approximately, how much gas liquor should be used to neutralize a convenient amount, say 15 cc., of chamber sulfuric acid.

Calculations. — Read the specific gravity spindle floating in the sulfuric acid and calculate, from the table on page 4, the amount of actual sulfuric acid in the 15 cc. to be used. From the equation,

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4,$$

find out how many grams of ammonia are necessary to unite with this amount of acid.

Ascertain the strength of the gas liquor and compute the volum necessary to contain the desired amount of ammonia.

For example: If 30 grams of ammonia (NH_3) are desired and the gas liquor is 8 per cent ammonia, there will be $\frac{10}{0.08} = 125$ grams required. The density of gas liquor being nearly the same as water, 125 cc. in place of 125 grams may be considerd the correct amount.

Enter the results as given below and have them verified by an instructor.

Amount of actual acid in 15 cc. of chamber acid,..grams.
Amount of ammonia equivalent to the acid, ...grams.
Volum of gas liquor to contain the ammonia,.....cc.

Procedure — Arrange a distilling apparatus consisting of a flask of a capacity of from 500 to 1000 cc. carrying a two-hole rubber stopper. Thru one hole put a thistle tube reaching to within 1 cm. of the bottom of the flask, thru the other hole insert a bent tube carrying a one-hole stopper fitted to a condenser. Put 15 cc. of chamber sulfuric acid into a 250-cc. gas bottle and adjust to the delivery tube of the condenser so that the bottle rests on the desk and the delivery tube dips under the acid. Draw from 10 to 50 cc. more than the calculated amount of gas liquor, — the amount depending on its strength, — pour it thru the thistle tube into the flask and begin heating. As soon as the distillation is well under way, look for the deposit of ammonium carbonate in the condenser. If any appears — as it always does — it will be necessary to break up this compound in the flask by adding lime. To do this make a paste of 10 to 15 grams of lime and 50 to 75 cc. of water and pour the mixture, which is milk of lime, thru a

piece of cheese cloth placed over the thistle tube. The reaction results in the precipitation of calcium carbonate in the flask,

$$CaO_2H_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_3 + 2H_2O,$$

and the liberation of ammonia which volatilizes faster than the ammonium carbonate.

When the sulfuric acid is entirely neutralized, as is shown by the action of litmus paper or a decided change in the appearance of the distillate, disconnect the apparatus. Filter the solution of ammonium sulfate in the gas bottle if tarry matter has collected in it, first making sure that all the ammonium sulfate is in solution, and evaporate the clear filtrate in a porcelain dish to the point of crystallization.

Cool the mixture, bring the mass of crystals on a paper filter and allow them to drain and further dry by pressing between filter papers. Weigh the crystals and enter the amount in the notebook.

To become familiar with the properties of the salt, heat a little in a dry test tube and hold a piece of moistend red litmus in the mouth of the tube. Ammonium sulfate melts at 140°; at 280° it decomposes, losing ammonia and leaving behind ammonium acid sulfate.

NOTES

The time of the student is such an important factor that considerable more than the required amount of ammonia is recommended for use. This obviates waiting for all the ammonia to be driven off and also saves evaporation of the increased amount of water which would distil over. Of course a waste of ammonia results. Industrially such a waste of ammonia would not be allowd.

If the evaporation procedes beyond a certain point the mass upon cooling will be solid salt. In this case filtering and drying are unnecessary. The danger in using this quicker method of drying lies in the fact that the solution of ammonium sulfate in water upon being heated to dryness passes over into a clear molten anhydrous mass so quickly that the change may not be noticed. Heating this molten anhydrous mass results in the decomposition of the salt as explaind in a previous paragraf.

In the manufacture of coal gas, by heating soft coal much of the nitrogen present is combined with hydrogen forming ammonia. Some of the oxygen that enters the retorts as they are charged combines with the carbon forming carbon dioxid. This weak acid, carbonic acid, unites with the weak base

ammonia and forms the volatil salt, ammonium carbonate. Part of the process of purification of coal gas consists in washing out the ammonia and ammonium carbonate in water. This wash is known as dilute gas liquor ($2\frac{3}{4}$ oz. of ammonia to the gallon) and may be concentrated by distillation. Such a concentrated product contains the equivalent of about 18 oz. of ammonia (NH_3) per gallon of liquid.

The United States normally produces about 300,000 tons of sulfate of ammonia annually. Since the war the production has doubled and is constantly increasing. It is a plant food furnishing both nitrogen and sulfur; excessive use as a fertilizer, however, may deplete the soil of its calcium.

The milk of lime which decomposes the ammonium carbonate must be straind or the lumps will clog the thistle tube. In place of the procedure described the mixture may be allowd to settle four or five seconds after stirring and the upper portion pourd thru the thistle tube leaving the lumps behind on the bottom of the container.

Should the process of distillation be interrupted before the sulfuric acid is neutralized the product will be a mixture of the neutral and acid ammonium sulfates.

Sometimes the tarry materials exist in the

neutralized solution in colloidal condition and are not flocculated until the ammonium sulfate solution has become more concentrated. Should flocculation occur during the course of evaporation the tarry substance then may be filterd out. It is this material left in the preparation which gives the peculiar brownish color to commercial sulfate of ammonia.

The point of crystallization is determind by blowing across the surface of the hot liquid. When a scum appears at once the evaporation by flame may cease.

QUESTIONS

(To be answerd in the notebook.)

1. How many grams of ammonia in 2 kilos of a solution containing 28.33%?
2. How much ammonia in 250 cc. of a solution of a sp. gr. of 0.970 containing 7.31% of NH_3?
3. How many tons of ammonium sulfate could be made from a tank car of concentrated ammonia containing 5000 gallons of 14% NH_3? The weight of a gallon may be taken as 8 pounds. What is this worth at $60.00 per ton?
4. What is the per cent of ammonia in ammonium sulfate?
5. Write the reactions, giving the names, showing how two different salts may be made by putting together ammonium hydroxid and sulfuric acid.
6. What other substances in addition to ammonia are produced by distilling soft coal?

7. What is the use of the lime in the distillation of gas liquor?

8. Explain the presence of ammonium carbonate in gas liquor.

9. Why is commercial sulfate of ammonia brown?

10. Why does a brown substance sometimes settle out during the concentration of the ammonium sulfate solution?

POTASSIUM NITRATE

Potassium nitrate is made by metathesis of potassium chlorid and sodium nitrate, taking advantage of the different solubilities of the four possible salts in hot and cold water.

Procedure. — Heat 200 cc. of water in a porcelain dish and when hot add 100 grams of sodium nitrate and 90 grams of muriate of potash. Evaporate until the volum is reduced to about 100 cc., and filter off the sodium chlorid, sand and dirt thru a carefully prepared Witt filter. Throw away the residue on the filter, and cool the filtrate until the crystals of potassium nitrate appear in quantity.

Some care is required to judge when the solution is boild down to one-half its original volum. If it is filterd too soon, in which case few or no potassium nitrate crystals separate out of the filtrate on cooling, the filtrate should be evaporated further and again filterd to remove the sodium chlorid which will separate as solution boils away. If the mixture boils too long before filtering the crystallization of the potassium nitrate will take place in the funnel stem and clog the filter. In such a case the whole mass should be put back in the dish with about 50 cc. more of water and reheated. It sometimes aids the filtering to warm

the funnel just previous to using. This can be done by pouring a test tube of hot water thru the funnel. Empty out the water.

Filter off the crystals of potassium nitrate when the solution is cold; set the crystals aside. Evaporate the filtrate again until reduced about one-half its volum, or until crystals of sodium chlorid appear in quantity, filter thru the Witt plate, rejecting the sodium chlorid on the filter and cool the filtrate to the lowest point possible to crystallize the potassium nitrate. Filter off this crop of potassium nitrate, and put with the quantity previously obtaind. As both crops of crystals came from a solution saturated with sodium chlorid as well as potassium nitrate and as sodium chlorid is slightly less soluble (4 grams per 100 cc.) in cold water than hot some sodium chlorid crystals will have formd on the nitrate. To get rid of these, dissolv the nitrate in hot water, using about 50 cc. or less for every 100 grams of crystals, and cool in cold water as was done before. Filter. The mother liquor should contain all the sodium chlorid and if the mother liquor adhering to the crystals on the filter can be replaced by water before they dry out the product will be free from chlorid. Wash the crystals with cold water, a drop at a time, until a few of the

crystals in water in a test tube give no test for chlorin ions when a soluble silver salt is added.

The microscope can be used to advantage here. If square right angle blocks (sodium chlorid) are formd adhering to the long nitrate bars the crystals will have to be redissolvd. If no blocks of sodium chlorid are seen it may be taken for granted that purification may be brot about by continued, drop by drop, washing with cold water. The crystals when pure may be dried by pressing between filter paper or by allowing to stand over one exercise.

NOTES

The Witt filter consists of a perforated porcelain disk in a funnel fitted into a heavy glass suction flask, having connection with an aspirator. It is a convenient and rapid means of filtering when properly used. The student should be supplied with paper filters of a diameter about one centimeter greater than that of the porcelain plate. Should the plates become chipt they can still be used if a small piece of filter paper is torn off and laid over the damaged place. Unless the chipt place is so closed pressure will make a hole in the filter paper allowing the precipitate to pass thru into the filtrate.

The flask should be supplied with rubber tubing of ordinary thickness, not pressure

tubing, and a pinchcock to help regulate the pressure. The proper use consists in arranging the apparatus, starting the pump, emptying the mixture on the filter, closing the rubber tube with the pinchcock and then shutting off the water. As the vacuum in the flask is relieved it can be increased by starting the pump and momentarily opening the pinchcock. Too much use of the pump is to be avoided.

It is only in exceptional cases where potassium nitrate is of agricultural importance. True, it contains both potash and nitrogen in one compound and therefore in concentrated form, but these substances are as well supplied in agriculture by the sodium nitrate and the potassium chlorid separately. In isolated localities where the freight rate is exceptionally high it is possible that the cost of manufacture of potassium nitrate would be less than the freight on the sodium chlorid eliminated in the process. In such a locality it might be desirable to use potassium nitrate for fertilizer.

The classic use of potassium nitrate is for black powder. Sodium nitrate being hygroscopic does not make a powder suitable for use in fire arms; however a coarse blasting powder is made from it, the large grains being glazed to keep out moisture.

When the two salts are dissolvd in water all four ions, K^+, Na^+, Cl^-, NO_3^-, exist as well as all possible combinations of these. As water evaporates the least soluble combination of ions, sodium chlorid, will come out of solution first, so that the reaction procedes by metathesis,

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

It is to be noted in this reaction that as the Na and Cl ions form the least soluble substance so do the two ions remaining after these unite, K^+ and NO_3^-, form the most soluble combination. Either circumstance would be sufficient to determin the direction of the reaction.

The change in solubility of the potassium nitrate in hot and cold solution is very great. When hot potassium nitrate is many times more soluble than sodium chlorid; at 33°, their molar solubilities are equal and below that temperature potassium nitrate is less soluble, being about one-half that of sodium chlorid at 10°.

A graphic representation of the solubilities of these salts will be of aid to the student. Such figures are found in the following texts: Kahlenberg, p. 435; Alexander Smith, p. 131; Blanchard, Synthetic Inorganic Chemistry, p. 26.

QUESTIONS

(To be answerd in the notebook.)

1. How many grams of potassium chlorid are required to unite with 100 grams of sodium nitrate? Keep one decimal place in the figure.

2. Of what use is potassium nitrate?

3. Write the symbols of the four salts that exist in solution at the beginning of this experiment. Write symbols for the ions.

4. What is the solubility of potassium nitrate at 100°? of sodium chlorid?

5. What is the solubility of these two salts at room temperature or the temperature of hydrant water? State the exact temperature selected.

6. Describe a test for chlorid ions.

7. Describe the crystals of potassium nitrate; of sodium chlorid.

8. When might it be desirable to use potassium nitrate as a fertilizer?

9. Where is sodium nitrate found? What is its common name? Why is it not used for making gun powder?

10. If one kilo of a solution of salt saturated at 100° is coold to 10° how many grams of salt will separate out? Consult the grafs in one of the references given in the last paragraf before the question.

POTASH SALTS

PART I

SULFATE OF POTASH-MAGNESIA

The sulfate of potash-magnesia is made according to the equation,

$$3KCl + 2MgSO_4 \cdot H_2O + 11H_2O = K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + KCl \cdot MgCl_2 \cdot 6H_2O,$$

by mixing saturated brines of potassium chlorid and magnesium sulfate.

Procedure. — Weigh out 60 grams of muriate of potash and add it, as fast as it will dissolv, to about 100 cc. of boiling water. Making sure that all the salt is in solution filter the mixture while hot through a Witt plate to separate the iron oxid, dirt and sand. Put the filtrate in a beaker, keep the liquid at boiling temperature, and concentrate the brine until crystals of potassium chlorid begin to appear on the surface, showing that the solution is saturated at that temperature.

While the foregoing is in operation weigh out 100 grams of kieserit and dissolv it in about 75 cc. of boiling water, adding the salt slowly. In case it does not all go into solution, indicated by a residue of salt on the

bottom of the beaker and a scum on the surface of the liquid, add 10 or 20 cc. more of water and heat, repeating the addition of small amounts of water and heating, if necessary, until the magnesium sulfate is all dissolvd. Filter, using the Witt plate, and concentrate the clear filtrate until the liquid is saturated as indicated by the formation of a scum on the surface. Mix the two hot saturated salt solutions and set the mixture aside for at least twelve hours. Both the solutions must be saturated upon mixing or the experiment will be a failure. The crystals that begin to form upon putting the solutions together and which further separate on cooling are the double sulfates of potassium and magnesium, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, sometimes cald the sulfate of potash-magnesia.

After the mixture has stood, filter off the crystals, drain them well on a Witt plate, transfer them to a paper and weigh. Save the filtrate which contains a solution of artificial carnallit.

The crystals of double sulfate may be dried in a few hours by spreading on paper when the exact weight may be obtaind or the approximate weight may be had at once, assuming that 5 to 6 per cent of the weight is water adhering to the crystals.

PART II

SULFATE OF POTASH, HIGH-GRADE

It is customary to make sulfate of potash from the double salt by adding sufficient potassium chlorid to carry on the following reaction:

$$3KCl + K_2SO_4 \cdot MgSO_4 \cdot 6H_2O = 2K_2SO_4 + KCl \cdot MgCl_2 \cdot 6H_2O.$$

Procedure. — Calculate the amount of potassium chlorid necessary to react with the amount of double salt at hand, and weigh out enuf muriate of potash to furnish this amount of actual salt, allowing for impurity. Heat the necessary amount of water to boiling, dissolv the salt, filter off the dirt on a Witt plate, and heat the filtrate until it is saturated all as previously described under sulfate of potash-magnesia.

Add the sulfate of potash-magnesia to boiling water, using 100 cc. for every 80 grams of salt, and put this mixture with the hot saturated solution of the chlorid. Potassium sulfate begins to separate at once and continues to come out on cooling. After standing 24 hours the salt may be filterd off

and dried in the air. Record the weight of dried salt.

The filtrate, which should be saved, also contains the double chlorids of potassium and magnesium (carnallit) similar to that obtaind under Part I.

PART III

MURIATE OF POTASH

Procedure. — Put the two filtrates containing the artificial carnallit brine together and evaporate the water until the hollow octahedral crystals of potassium chlorid appear in abundance. The decomposition of the carnallit yields some potassium chlorid which crystallizes out first; this is rapidly followd by the clear dense crystals of the carnallit itself. The latter may compose the major portion of the precipitate. If too much or nearly all the water is evaporated off magnesium chlorid will separate out making the product deliquescent. The crystals may be separated from the magnesium chlorid brine by the use of the Witt plate. The filtrate containing the solution of magnesium chlorid may be thrown away.

The two salts, sulfate of potash and muriate of potash, dried and weighd, are handed in separately.

NOTES

The amount of water used to dissolv the salts may be quite a little more than would be calculated from the solubility

tables. There are several reasons for this. First, there are impurities present which if they contain an ion in common with the principal salt may necessitate the use of more water. To illustrate this suppose there are 10 grams of sodium chlorid in every 50 grams of the crude potassium chlorid (a chlorid ion in common), then it is necessary to furnish water for the sodium chlorid as well as for the potassium chlorid; while if 10 grams of calcium nitrate were present (no common ion: K^+, Ca^+, NO_3^-, Cl^-) this substance would dissolv in the solution already saturated with potassium chlorid. Second, sufficient water should be present so that the solutions may be filterd before they approach saturation; otherwise the crystallization that results on cooling clogs the filter and causes delay.

In filtering all such mixtures which contain fine sediment, first allow them to settle and bring the solid matter onto the filter only at the end of the operation after the clear liquid has past thru the filter.

Kieserit, the magnesium sulfate with one molecule of water, is the salt that has separated out in the German deposits. Ordinarily from water the heptahydrate, $MgSO_4 \cdot 7H_2O$, separates out. Epsom salts, the heptahydrate, are made from kieserit by dissolving kieserit and allowing the salt to crystallize.

In all this work it is the object to precipitate a salt by mixing two hot saturated solutions. The appearance of crystals or a scum (film of fine crystals) on the surface may be taken as an indication of saturation. Mixing solutions which are not saturated may result in large loss of the desired substance. Often the addition or withdrawal of one cubic centimeter of water is all that is necessary to produce the condition sought.

In dissolving the double sulfate in water the salt may not appear to dissolv completely. This is immaterial as the residue is potassium sulfate, the same as the desired product. It is possible to crystallize out potassium sulfate by evaporating the solution of potash-magnesia sulfate.

Muriate of potash is sold in three grades containing 80, 95 and 98 per cent, respectively. The material containing 80 per cent potassium chlorid is the grade mostly used for fertilizers. This is produced industrially by treating the raw salts as they are mined with a hot saturated solution of magnesium chlorid such as is thrown away at the end of this experiment. The resulting hot solution is coold in cement tanks and the crude muriate of potash separates out. The crystals are centrifuged and further dried over a fire in sloping pans about 10 × 60 feet in

size. Bromin is obtaind from the magnesium bromid in the spent magnesium chlorid brine.

In former years one of the salts mined extensively in Germany was carnallit in a high degree of purity. Such deposits are no longer available, and in its place the carnallit brine appears from which the high grade, 96 to 98 per cent, muriate of potash is made by concentration and crystallization.

The American sources of potash which have been investigated since 1908 and developed since the war are the giant kelps of the Pacific coast, the nativ potash-bearing rocks, the products of blast furnaces and cement kilns and the salts of inland lakes. A brief discussion of each source is given.

The kelps exert a selective action on the salts in the sea and take up relatively more potassium chlorid than other compounds. When the kelp is dried and incinerated the ash contains 15 to 50 per cent muriate of potash. The cost of production is so high, however, that the procedure is not economical. On the other hand an ingenious fermentation process has been devised, producing acetone and esters as the principal products and potash as a by-product. This is in successful operation on the Pacific coast.

The amount of potash in such minerals as

feldspar is unlimited, but here again the cost of production is so great that little potash is, as yet, produced from this source. Another mineral containing large quantities of potash is found in Utah and called alunite. This substance contains silicates and sulfates of potassium and aluminium which on heating furnish water soluble sulfate of potash. Six hundred tons a month of potassium sulfate were being produced in 1918 from this source.

Potash is being produced in this country, England and France from the blast furnaces of the steel industry. The limestone, iron ore, and coke used in the smelting may each contain some potash; if so during the heating some of this is volatilized. Special devices, electrical precipitators, take the potash-bearing dust out of the gases as they pass from the furnaces. Potassium chlorid is the substance obtaind. As there is generally insufficient chlorin to combine with the potassium the amount of substance volatilized is limited by the chlorin available. The addition of common salt, sodium chlorid, to the furnace charge consequently increases the amount of potash recoverd. It is said that there is sufficient potash available from this source to furnish the entire needs of this country.

The cement kilns also volatilize potassium

chlorid from potash compounds present in the limestone and silicates used in their manufacture. The material is very fine and would be lost as " smoke " if the particles were not charged with electricity and then caused to deposit on strong electrically charged plates in the Cottrell process of electrical precipitation.

Searles Lake in the California desert contains over 12 square miles of a crystal deposit 70 feet thick. These crystals are surrounded by a saturated brine carrying about 5 per cent of potassium chlorid. The brine contains two bases, sodium and potassium; and four acids, chlorides, sulfates, borates and carbonates. Potassium chlorid and borax are the products of this industry. It is calculated that there are 30 million tons of potash in this region which in itself is sufficient to supply the needs of America for 25 or more years.

The work outlined in this exercise deals with double salts occasiond by the presence of magnesium when the magnesium is absent, as in most of the American deposits, the process of crystallization is much simplified.

The size of the crystal generally varies with the rapidity with which it forms. If the salt forms quickly, the crystals are small; if more slowly, the crystals are larger.

Each of the crystals has its definit shape which is easily seen under the microscope. Reference is given to various figures of crystals in Watt's Dictionary of Chemistry, Vol. II, pages 148 ff.

The hydrated double sulfate of potassium and magnesium is inclined to form coarse monoclinic prisms which look like half cubes or diamonds which have been prest so that the upper faces are not directly over the lower ones. Compare Figs. 285 and 287.

Potassium chlorid, like sodium chlorid, appears in cubes or colums, or commonly as a four-sided funnel or hollow pyramid.

Potassium sulfate may be in small hexagonal prisms (really rhombic) or in longer prisms with a bluntly tapering end. Vid. Figs. 272 and 297. Similar figures are shown in Gmelin-Kraut, Vol. 2_1, p. 49.

Magnesium sulfate is inclined to grow in long needles (rhombic) with faces on the very abrupt end. Vid. Fig. 281.

Magnesium chlorid, $MgCl_2 \cdot 6H_2O$, forms monoclinic prisms much like the double sulfate of potash-magnesia. Vid. Figs. 285 and 287.

QUESTIONS

(To be answerd in notebook.)]

1. Calculate the per cent of potash, K_2O, in the sulfate of potash-magnesia; in potassium sulfate; in potassium chlorid. Express results as follows:

$$\frac{K_2O}{K_2SO_4} = \frac{94.3}{174.4} = 54.1\%.$$

2. Tell when a solution is saturated.

3. How many pounds of potassium chlorid in a ton of muriate of 80 per cent grade?

4. How much potash is there in a ton of kainit containing 12 per cent K_2O?

5. If potassium chlorid and magnesium sulfate solutions are mixt what salt is most likely to be precipitated? Why?

6. What is the solubility of four salts used in the exercise? Express relatively at some definite temperature, putting the most soluble at the head of the colum.

7. What materials, in addition to sodium chlorid, go to make up the 20% impurities in ordinary muriate of potash?

8. How does the double sulfate of potash-magnesia decompose upon being dissolvd in a small quantity of water?

9. What use is made industrially of the magnesium chlorid brine that, in this exercise, is thrown away after the high-grade muriate of potash has been filterd off?

10. Describe the American sources of potash.

LEAD NITRATE

Lead nitrate is made from litharge, PbO, and nitric acid.

Calculation. — From the equation,

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O,$$

calculate the amount of nitric acid required to act on 20 grams of lead oxid. Read the spindle floating in the nitric acid to be used and, by reference to the table at the end of this exercise, ascertain how many grams of actual nitric acid in one cubic centimeter of this liquid. By division find out how many cubic centimeters of this nitric acid must be used.

Enter the results in the following form:

Nitric acid required, grams,.....
Density of nitric acid solution,.....
Number grams nitric acid in 1 cc.,.....
Volume of nitric acid solution, required, cc.,.....

Procedure. — Weigh out 20 grams of litharge, and place it in a small beaker with the required amount of nitric acid. Heat until the oxid is converted to nitrate and solution results, adding more water, if necessary, to dissolv the crystals of lead nitrate.

If a white precipitate of lead sulfate is present the mixture must be filterd to remove the lead sulfate. Heat the filtrate, or the clear solution, in case filtration was not necessary, until it is saturated; then either cool the solution rapidly or allow it to stand until the next exercise. The lead nitrate crystals may be filterd on an ordinary filter or on a Witt plate and dried in the open air. If the amount of mother-liquor (filtrate) is considerable more crystals may be obtaind by continuing the evaporation of the liquid.

NOTES

It is essential that the apparatus be clean. If sulfates are introduced by means of the measuring cylinders or beakers white insoluble lead sulfate will be formd which must be filterd out. If commercial nitric acid is used it may contain sulfuric acid.

If the litharge does not all dissolv more nitric acid may be added or the solution may be filterd and the excess litharge discarded. An excess of nitrate ions from the acid reduces the solubility of the lead nitrate in water so it is difficult to use solubility tables to determin the least volume of liquid necessary to hold the amount of lead nitrate produced in solution.

The amount of lead nitrate in 100 cc. of a

solution saturated at given temperatures is found in the following table.

SOLUBILITY TABLE

Temperature	0°	10°	18°	25°	50°	100°
$Pb(NO_3)_2$ grams	36	44	51	56	79	127

STRENGTH OF NITRIC ACID SOLUTIONS

Density.	1 cc. contains nitric acid, grams.
1.05	0.094
1.10	0.188
1.15	0.2177
1.20	0.388
1.25	0.486
1.30	0.617
1.35	0.753
1.40	0.914
1.45	1.121

QUESTIONS

(To be answerd in the notebook.)

1. How many grams of lead nitrate could be made from 20 grams of litharge? What amount of boiling water is necessary to dissolv this amount of salt? (See solubility table.)

2. How many grams of lead nitrate did you make?

3. Is the salt more or less soluble in nitric acid than in water? Why?

4. How many cubic centimeters of nitric acid of a density of 1.10 would be necessary to measure out if 200 grams of actual acid were required?

5. How is nitric acid made? Explain the presence of sulfuric acid in commercial nitric acid.

LEAD ARSENATE

Lead arsenate is the standard arsenical poison for chewing insects. It is made by mixing equivalent amounts of solutions of either lead acetate or lead nitrate with sodium arsenate.

Calculation. — Inquire as to the character of the sodium arsenate available — as to its condition of hydration and degree of purity — and from the equation,

$$Na_2HAsO_4 \cdot 7H_2O + Pb(NO_3)_2 = PbHAsO_4 + 2NaNO_3 + 7H_2O,$$

calculate the amount of disodium hydrogen arsenate that will be necessary to react with 20 grams of lead nitrate.

If the salt is hydrous the $7H_2O$ will be weighd out and must be calculated; if anhydrous the $7H_2O$ must be left out of the calculation. If the salt is 80 per cent pure the amount to be used must be increased by dividing by 0.80.

Dissolv the lead nitrate in 50 cc. of warm water and dilute to a total volum of 350 cc. with cold water. Similarly dissolv the requisit amount of arsenate of soda in a little warm water and dilute to 350 cc. with cold

water. Mix the two solutions. Test the liquid with pieces of red and blue litmus paper.

As the precipitate of white lead arsenate settles decant the clear supernatant liquid — best over the edge of the beaker, not using the lip — fill the beaker with fresh water, stir the mixture and again allow the precipitate to settle. Repeat this washing until the soluble salts are removed, and the precipitate, becoming colloidal in character and refusing to settle completely, is partially dispersed thru the liquid.

This condition being reacht allow the mixture to stand over night, so that as much as possible of the lead arsenate will settle out, then decant most of the liquid, neglecting the loss of the comparatively small amount of precipitate in colloidal condition, and bring all the remaining precipitate gradually onto one 15-cm. filter folded in the ordinary way. Allow the precipitate to drain in the funnel for several days; even a week, as a rule, is not too long.

When the amount of moisture is reduced to about 50 per cent the mass will separate easily from the paper and should be handed in.

NOTES

With large beakers such as are most always used in this washing process it is an easy matter to put a stirring rod thru the bottom or sides of the beaker. The student should learn to stir without touching the stirring rod to the beaker. In such a case as the one in hand the stirring is best done by the force of the entering wash water.

The quality of the sodium arsenate on the market varies greatly. The best grades are crystallin and hydrated. The inferior grades are frequently anhydrous, massiv, of spongy appearance and carry considerable sodium carbonate and sulfate.

If the two salts are not used in equivalent proportions the litmus paper will show which was taken in excess. Lead nitrate turns the paper red while sodium arsenate turns it blue.

The washing takes out the excess of either salt that may have been used, and the sodium nitrate formd by the reaction. In the presence of any considerable quantity of these salts the small particles of lead arsenate are flocculated, that is, many thousands are brot together in one floc. As the concentration of the soluble salts is lowerd by washing the particles separate, are deflocculated,

and become so small that their rapid motion ofsets the force of gravity.

The rapid motion of any small particle in suspension may be easily observd under a high power microscope. The motion is produced by the molecules of water which strike the larger particles with sufficient force and frequency to keep them in oscillation. This motion is known as the "Brownian movement."

The action which the arsenate of lead undergoes in becoming colloidal is said to be as follows: When the soluble salts (electrolytes) are sufficiently decreased by the washing process some groups of molecules of lead arsenate react with either the hydrogen or the hydroxyl-ions of the water combining with them. If the particles combine with the hydrogen they become positively charged colloids and the liquid retaining the negativ hydroxyl group becomes negativ. It is entirely possible that it is the layer of atoms on the surfaces of the particles of arsenate of lead which is active in combining with either the H^+ or the ^-OH of the water. The action of salt in coagulation, or precipitation, consists in neutralizing the electrical charges. As this takes place the lead arsenate particles, which were previously all of the same electrical condi-

tion and consequently were all repellent of each other, gradually floc together, the Brownian motion slows down, and as the particles continue to coalesce the Brownian motion ceases and the solid separates out as a precipitate.

The arsenate of lead formd is a mixture of two compounds; one acidic having the symbol $PbHAsO_4$, and one basic represented by the formula $Pb_3As_2O_4 \cdot Pb_2OHAsO_4$. These two compounds are in equilibrium,

$$5PbHAsO_4 + HOH \rightleftarrows Pb_5OH(AsO_4)_3 + 2H_3AsO_4,$$

the acidic one being gradually changed to the basic one as the arsenic acid formd in the reaction is decanted off during the washings. The change to the basic compound, however, is very slow as with very slight concentrations of arsenic acid such as accumulate in the wash water the action stops and no more basic compound is formd until the supernatant wash water is replaced by fresh. As an example of the slowness of the change it required, in an experiment by McDonnell and Graham of Washington, D. C., continuous washing for a year to change two grams of the lead acid arsenate to the basic substance.

A piece of blue litmus paper added to the

mixture after the material has been well washt will turn red slowly showing the presence of a slight concentration of acid. This is the arsenic acid hydrolyzed off from the acid arsenate.

The addition of any acid changes the equilibrium from right to left forming the acidic arsenate with the elimination of the basic compound. Most of the lead arsenate pastes on the market are made with lead nitrate and the acidity of the system is sufficient to produce a mixture consisting mostly of the acid arsenate with smaller proportions of the basic compound.

Inasmuch as the acidic arsenate consists of approximately 33 per cent As_2O_5 and the basic approximately 23 per cent the analysis of the compound will show the proportions of the two arsenates present. For example, a mixture of the two analyzing 30 per cent As_2O_5 is nearly all acidic and contains very little of the basic compound, while one analyzing 28 per cent is composed of equal parts of the two arsenates, basic and acidic. These facts can be applied to the analysis of two commercial samples of arsenate of lead which are here given, one made from lead nitrate which contains a strong acid and the other made from lead acetate containing a weak acid.

ANALYSES OF LEAD ARSENATE

	Made from lead nitrate, per cent in dry salt.	Made from lead acetate, per cent in dry salt.
As_2O_5....	31.40	25.40
PbO.....	62.80	74.11

It will be seen that both preparations are mixtures of the two compounds, the one made from lead nitrate containing much more, in fact is nearly all, of the acidic compound $PbHAsO_4$, while the one made in the presence of less acid contains a large proportion of the basic compound.

Most of the arsenate of lead on the market is in the form of a paste containing 45 to 50 per cent water, consequently the actual per cents of arsenic and lead oxids in the materials would be about one-half the figures just given. The dry powder on the market is said to be made by an entirely different process, by suspending lead plates in arsenic acid and causing chemical action by means of an electric current. The lead arsenate that falls off the plates has only to be washt and dried.

For most uses lead arsenate replaced Paris green as an arsenical poison. Its two advantages are its greater insolubility and its ability to stick. The solubility of lead arsenate in

pure water is extremely slight. It is, however, readily decomposed by the salts which appear in natural waters, the carbon dioxid of hard water being particularly effective. The amounts of arsenic acid set free by this reaction are, generally, less than one per cent, depending on the water used and not enuf to burn foliage.

QUESTIONS

(To be answerd in the notebook.)

1. How many grams of anhydrous, 80 per cent pure, arsenate of soda would be required to put with 20 grams of lead nitrate?
2. Explain how lead nitrate can turn litmus red.
3. Similarly, how sodium arsenate can turn litmus blue.
4. What is meant by the terms flocculent; deflocculated?
5. Explain the action of soluble salts in flocculating the precipitate.
6. What salts are washt out of the mixture? How did the litmus paper act in your preparation immediately after mixing?
7. How much arsenic acid (As_2O_5) in an ordinary lead arsenate paste?
8. If lead costs more than arsenic which is cheaper to use as a lead salt, the nitrate or the acetate? The analyses of lead arsenates given will furnish the answer.
9. Calculate the per cents of As_2O_5 and PbO in $PbHAsO_4$ in the basic compound. This will be confusing unless the student keeps in mind the fact that the amount of two arsenics cannot be calculated where only one exists, *i.e.*, As_2O_5 cannot be calculated from

one molecule $PbHAsO_4$, whereas it can from two molecules. In other words the student is askt to resolv $2PbHAsO_4$ into $2PbO$, As_2O_5 and H_2O, the water being neglected in this case.

10. What are the advantages of lead arsenate over Paris green?

LIME-SULFUR

36-80-50 Formula

Lime-sulfur is an amber colord liquid containing calcium polysulfids, CaS_4 and CaS_5, and some calcium thiosulfate, CaS_2O_3. It is made by boiling lime with a suspension of sulfur. It first came into use as an insecticide on the Pacific coast about 1900 to combat the San José scale. Previous to that time a "Lime, Sulfur and Salt" mixture had been used as a sheep wash. Nowadays its use in more dilute solutions is extending rapidly to control "blights" or fungus diseases, while the stronger solution is still one of the standard remedies for scale insects. In the stronger solutions it is appl'ed during the late winter or early spring before the buds burst.

Procedure. — Select a beaker or porcelain dish of 400–500 cc. capacity, measure into it 200 cc. of water, and mark the level of the liquid so that the mark can be recognized after the dish is used for bo'ling. Weigh out 38 grams of quicklime, and slake it in the proper amount of water. Weigh out 80 grams of sulfur flour and make this into a *thoroly* moistend paste with about 200 cc. of

water. Bring the ingredients together in the markt dish, place the dish on a piece of asbestos over a flame, and keep the mixture boiling gently.

During the boiling replace the water if it gets near the 200 cc. mark. It is not necessary that any particular volum should remain at the end of the boiling period; the less water the stronger the solution and the more thiosulfate is decomposed and the more CaS_5 is formd in place of CaS_4; however, if the solution is made too concentrated there will not be sufficient liquid to float the hydrometer spindle. To make a solution of the same density as the commercial preparations, 34° Bé., it would be necessary to concentrate the liquid to less than 200 cc.

When the liquid acquires a dark amber color and the suspended sulfur has disappeard the lime-sulfur is made. This may require an hour. If the preparation is to stand until the next exercise it should be coverd to keep out as much oxygen as possible. Reducing the surface by placing the mixture in a narrow vessel also reduces the oxygen absorption. If it is intended to complete the work at once the mixture may be coold by immersing the container in water. After standing observe that a crust has formd on the surface of the liquid which is

much thicker if the preparation has stood for several days. Decant the clear liquid into the special lime-sulfur hydrometer cylinders and take the density on both the specific gravity and Beaumé scales. From the concentrated clear liquid prepare two sprays, one for use when the buds are dormant and one for use on the green foliage in summer. Take the density (Bé.) of both diluted sprays and record the data in the notebook.

If any lead arsenate is available make a thin paste of this and add some of it to the dilute summer spray. Notice the gradual darkening as some of the lead is withdrawn from the combination with arsenic acid and combined with sulfur to form black lead sulfid; small amounts of arsenic acid are set free at the same time. This is a combination spray having two functions, insecticidal and fungicidal.

NOTES

The 1910 Geneva Formula, 36 pounds of lime; 80 pounds sulfur; 50 gallons water, is here made over for laboratory use. The directions are based on bulletin No. 329 of the New York Agricultural Experiment Station, by Van Slyke, Bosworth and Hedges.

If the lime is pure 36 grams should be used, if 95 per cent CaO (*i.e.*, 5 per cent MgO)

38 grams should be used, if 90 per cent lime 40 grams. Lime that is over 10 per cent magnesium oxid should not be used as it is a waste of material. The magnesium forms insoluble compounds that go into the sediment. In case the lime is already slaked increase the quantity in the ratio of the weights of $CaO : CaO_2H_2$ (*i.e.*, 56 : 74).

It is an easy matter to select lime that carries less than 2 per cent of magnesia as the analysis is on the barrel and the product of a given lime-kiln is fairly constant in composition.

If all the material is not in very finely divided condition it will remain as sediment and not react; hence the sulfur is moistend to prevent lumping.

If a beaker is used place a piece of asbestos under it, otherwise the solid material will form a blanket over the bottom of the beaker and prevent the diffusion of the heat. The glass will not stand sudden local heating and cooling resulting from such blanketing.

The reactions which take place when the material is being made, according to Professor Tartar at the Oregon Agricultural Experiment Station, are, first, the action of lime and sulfur to form calcium tetrasulfid, and calcium thiosulfate,

$$3CaO_2H_2 + 10S = 2CaS_4 + CaS_2O_3 + 3H_2O.$$

Second, as the liquid becomes concentrated the calcium thiosulfate breaks down forming the insoluble calcium sulfite liberating one atom of sulfur,

$$CaS_2O_3 = CaSO_3 + S.$$

This reaction may be taking place in this experiment when the volume of the liquid is reduced to about 200 cc. The insoluble calcium sulfite remains as a sediment. Third, the sulfur liberated from the thiosulfate unites with the tetrasulfid forming pentasulfid,

$$CaS_4 + S = CaS_5.$$

Thus the composition of the mixture changes during concentration. The amounts of thiosulfate and tetrasulfid become lessend and the quantity of pentasulfid increased. Such changes are considerd desirable and have been effected in most of the commercial preparations on the market.

Combination sprays may be made by mixing lime-sulfur with arsenate of lead or nicotine sulfate, or both, and simultaneously kill chewing insects and aphis, as well as prevent attacks of fungus diseases.

Professor Schaefer, of the Michigan Agricultural College, states that the action of lime-sulfur solution upon the San José scale is one of suffocation; that the caustic liquid

finds its way under the edges of the little shell under which the insect lives, shutting off the outside oxygen and rapidly consuming what remains inside.

The fungicidal action of lime-sulfur is thot to be due to the sulfur deposited from it. This, in the air, oxidizes slowly to sulfur dioxid which is toxic.

Long boiling exposed to the air, as is necessary in laboratory manipulation, is harmful to the product as the polysulfids react rapidly with the oxygen of the air depositing sulfur and forming thiosulfate,

$$CaS_3 + 3O = CaS_2O_3 + 3S.$$

This is the change that takes place when lime-sulfur stands exposed to the air. At first only a film of sulfur is seen as the calcium thiosulfate dissolvs, but as the upper layer becomes saturated with thiosulfate crystals these become mixt with the sulfur forming a hard crust. It is evident from this that the mixture should not stand in the laboratory any longer than necessary.

The action of lime-sulfur when used as a spray follows from the explanation in the previous paragraf. First, it rapidly takes up oxygen forming calcium thiosulfate and depositing all the sulfur in excess of two atoms to the molecule. Second, the thiosulfate

slowly breaks down to insoluble sulfid and one atom of sulfur is set free. This change is slow and is represented by the equation,

$$CaS_2O_3 = CaSO_3 + S.$$

LIME-SULFUR TABLE *

Data furnishing a basis for diluting lime-sulfur wash

Density.	Sulfur to 1° Bé., per cent.	Sulfur in sol., per cent.	Wt. one gal., lbs.	Sulfur in one gal., lbs.	Dilution as indicated for 1 gal. solution.		
					Dormant spray. (San José scale), gals. water.	Blister mite, gals. water.	Summer spray, gals. water.
36	0.75	27.00	11.08	2.99	9	12½	45
35	0.75	26.25	10.98	2.88	8¾	12	43¼
34	0.75	25.50	10.88	2.77	8¼	11½	41½
33	0.75	24.75	10.78	2.67	8	11	40
32	0.74	23.70	10.69	2.53	7½	10½	37¾
31	0.74	22.95	10.60	2.43	7¼	10	36¼
30	0.73	21.90	10.51	2.30	6¾	9½	34¼
29	0.73	21.15	10.42	2.20	6½	9	32¾
28	0.72	20.15	10.32	2.08	6	8½	31
27	0.72	19.45	10.23	1.99	5¾	8	29½
26	0.71	18.45	10.15	1.87	5¼	7½	27¾
25	0.70	17.50	10.07	1.76	5	7	26
24	0.69	16.65	9.98	1.65	4½	6½	24¼
23	0.68	15.65	9.90	1.55	4¼	6	22¾
22	0.67	14.75	9.82	1.45	3¾	5½	21¼
21	0.66	13.85	9.74	1.35	3½	5	19¾
20	0.65	13.00	9.67	1.26	3¼	4¾	18¼
19	0.65	12.35	9.59	1.18	3	4¼	17
18	0.65	11.70	9.51	1.11	2¾	4	16
17	0.65	11.05	9.44	1.04	2½	3¾	15
16	0.65	10.40	9.37	0.97	2¼	3½	14
15	0.65	9.75	9.30	0.90	2	3	12¾

* From Bulletin No. 329, page 316, New York Agricultural Experiment Station; Van Slyke, Bosworth and Hedges.

Third, the sulfite takes up oxygen forming calcium sulfate,

$$CaSO_3 + O = CaSO_4,$$

so that calcium sulfate and sulfur are the final products of decomposition of the lime-sulfur mixture.

The analysis of a commercial lime-sulfur concentrate is as follows:

Sp. gr., 1.30 or 33.7 Bé.

Sulfur in thiosulfate,	0.25%
Sulfur in tetrasulfid,	0.50%
Sulfur in pentasulfid,	24.75%
Total sulfur,	25.50%

This shows that the amount of thiosulfate has been greatly reduced, and that the substance present in greatest quantity is calcium pentasulfid.

QUESTIONS

(To be answerd in the notebook.)

1. Did you have sufficient lime-sulfur solution to float the hydrometer spindle? What was the Beaumé reading of your solution?

2. How many pounds of sulfur in one gallon of your solution?

3. How much would the sulfur in 50 gallons cost at the rate of $20.00 per ton?

4. What dilution did you make for the San José scale? What was the density of the dilute solution?

5. What dilution for summer spray? Resulting density?

6. What change was observd when lead arsenate was mixt with the summer spray? What new insoluble substance was formd?

7. What is the per cent of sulfur in the lime-sulfur you made?

8. What substances are in lime-sulfur? Underscore the one present in largest quantity.

9. What is in the sediment in lime-sulfur?

10. Write the reactions that take place when the lime-sulfur is made, placing the name of each substance under its symbol.

11. Similarly write the series of reactions that take place when lime-sulfur is oxidized.

12. What effect on the composition of lime-sulfur has long boiling? The concentration below 200 cc.?

13. What are the uses of lime-sulfur?

14. What is said to be the action of lime-sulfur in killing San José scale?

15. What are the final products of oxidation of lime-sulfur?

16. A barrel of lime-sulfur was left half full over one season. What substances would be found in the crust that formd on the liquid?

17. What specific gravity is equivalent to 33 Bé.?

18. What are the ordinary impurities in lime?

19. Write the reaction for slaking lime.

20. How many grams of slaked lime can be made from 40 grams of quicklime?

COPPER SULFATE

Procedure. — Place in a beaker 10 grams of metallic copper, 50 cc. of water, 15 to 18 cc. of chamber sulfuric acid and 25 cc. of dilute (sp. gr. 1.2, 32 per cent) nitric acid. Place the mixture on asbestos, under a hood, and heat gently with a low flame until the copper is all dissolvd. This should require about an hour. In case the solution becomes saturated during the heating as evinst by the crystals forming on the surface, add a few drops of water. When the copper is all dissolvd continue heating until the solution is saturated, then remove the beaker, place it in cold water and stir the solution as it cools until crystallization is complete. Filter off the crystals on a Witt plate. Evaporate the filtrate to the point of crystallization and cool the liquid until all the crystals have formd that will. If possible pour out the mother liquor, which consists mostly of strong acids, and bring the remaining crystals onto a Witt filter. Put both crops of crystals into 25 cc. of boiling water and adjust the quantity of water, by adding directly and boiling off, until the salt is all dissolvd and the solu-

tion becomes saturated. Cool the liquid with stirring or allow it to stand until the next exercise. Filter off the crystals and dry them between filter paper. Save the mother liquor for the tests which follow.

Tests for copper; Notebook. — Test some copper sulfate by adding ammonium hydroxid, at first one drop, then in larger quantity. The light blue insoluble substance formd by the small amount of ammonia is a basic copper sulfate; the blue solution contains copper and ammonia together in one ion, an ammonio-cupric sulfate $Cu(NH_3)_4SO_4$. This solution contains very few copper ions — only those that break away from this complex. The formation of a blue solution is a test for copper. To the blue solution add a few drops of potassium ferrocyanide. There being so few Cu ions the copper ferrocyanide formd is not v sible. Break up the ammonio-copper complex by adding acetic or dilute hydrochloric acids. As soon as copper ions are present in amount of about 0.002 per cent the copper ferrocyanide begins to be visible.

Add a few drops of potassium ferrocyanide to a copper sulfate solution. The formation of brown copper ferrocyanide is a test for copper.

NOTES

Bluestone or copper sulfate is the important salt of copper for agriculture. Its weak solution is fungicide and a disinfectant. Seed wheat is treated with it to kill the spores of the smut. Bordeaux mixture and Paris green are made from it.

Copper does not dissolv in acids without first being oxidized. This may be accomplisht, superficially, by heating in air when the resulting coating of black copper oxid will dissolv in sulfuric acid. Copper may be fused with sulfur when the resulting copper sulfid will respond to the action of sulfuric acid. The unreduced copper sulfid of copper matte which falls to the bottom of the tank when crude copper is electrolytically purified is used to make copper sulfate. Copper moistend with acid will take oxygen from the air and dissolv slowly. In this experiment the oxygen is obtaind from nitric acid.

QUESTIONS

(To be answerd in the notebook.)

1. From the symbol, $CuSO_4 \cdot 5H_2O$, calculate the amount of crystallized salt that may be made from 10 grams of metallic copper.

2. From the same symbol find out how many grams of sulfuric acid would be necessary.

3. Consult the table of the density of sulfuric acid under superphosphate and determin how many cubic

centimeters of sulfuric acid would be necessary to contain the number of grams found under 2.

4. What volum of nitrogen oxids was given off in this experiment? To solv this problem it will be necessary to establish the relationship between the weight of copper used and the volum of gas given off. The gas given off is the colorless nitric oxid which changes to the brown nitrogen dioxid without change in volum upon exposure to the air. The following equation shows the decomposition of nitric acid as it takes place in the experiment,

$$4HNO_3 = 2H_2O + 3O_2 + 4NO.$$

The change from the colorless to the brown oxid is simple,

$$2NO + O_2 = 2NO_2,$$

and the quantities 2NO and $2NO_2$ bear out the statement that there is no change in volum in the oxidation of nitric oxid to nitrogen dioxid. The relation of the nitrogen dioxid to the copper must be sought thru the oxygen which unites with the copper,

$$Cu + O = CuO.$$

The copper being once oxidized we lose interest in it, for the purposes of this calculation, as it reacts with the sulfuric acid without changing its relationship to the oxygen,

$$CuO + H_2SO_4 \cdot aq. = CuSO_4 \cdot aq.$$

Now it is possible to establish the relationship of the copper to the nitrogen dioxid thru the oxygen as follows: One Cu unites with one O, hence 6Cu unites with $3O_2$ and, from the first equation, the production of $3O_2$ is accompanied by the evolution of 4NO which goes to $4NO_2$ without change in volum. Then 6Cu are accompanied by the production of $4NO_2$

which establishes the relationship between the copper and the gas given off. The number of grams represented by the symbol NO_2 occupies 22.4 liters (molecular volum). Now we have the complete data for the ratio which is

$$\frac{6Cu}{4(22.4 \text{ liters})} = \frac{381.6 \text{ grams of copper}}{89.6 \text{ liters of gas}}.$$

As 10 grams of copper were used in the experiment the following proportion will give the number of liters of gas produced:

$$\frac{381.6}{89.6} = \frac{10}{x} = \text{liters of either NO or } NO_2.$$

5. What is necessary to make copper dissolv in acids?

6. What are the uses of copper sulfate?

7. What are two tests for copper? What compound in each case is used to recognize the copper?

8. How can the number of copper ions in a solution be reduced to a negligible quantity?

9. What oxid, or oxids, of nitrogen are red? What colorless?

10. How many liters of nitrogen dioxid were given off in this experiment? Of nitric oxid oxidized by the air? How many grams of each?

PARIS GREEN

Paris green closely approximates the formula $Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$, which was assignd it by Ehrmann in 1834, and is cald an aceto-arsenite of copper. There are two general processes for making it, first replacing most of the acetate ion of copper acetate by the arsenite ion of arsenious acid; and second, replacing some of the arsenite ion of copper arsenite by the acetate ion of acetic acid. The latter process is followd in these directions.

Procedure. — Dissolv 9 grams of dry carbonate of soda, or 24 grams of hydrous, in a beaker or porcelain d'sh in 80 cc. of water. Into this solution sprinkle gradually 16 grams of arsenious oxid, and boil until the acid has united with the soda as shown by solution of the resulting sodium arsenite.

Dissolv 20 grams of copper sulfate in 80 cc. of water. When both of the solutions are at about 60° — as warm as the hand can comfortably bear — pour the sodium arsenite solution into the copper sulfate. Add 10.5 cc. of 50 per cent acetic acid — or an equivalent of any other strength, and allow the

mixture to digest at about 50° for some time on a piece of asbestos board over a low flame. If the green copper aceto-arsenite does not form at this point, not enough acetic acid has been added. Consult an Instructor before adding more than a few drops of acid as too much may decompose the salt. Stir occasionally — once in five minutes — and when the reaction seems complete drain the green product on a funnel and wash to remove soluble arsenites and sodium sulfate. Examin the size and shape of the particles under a microscope. When dry put in a clean, dry beaker and see if it "flows" well.

NOTES

Paris green is one of the oldest arsenical insecticides. For many years it was the standard remedy for the potato beetle. It is applied to the vines suspended in water.

The composition of Paris green required by the symbol is never exactly attaind, the amount of arsenic being somewhat less than the ideal quantity. The analysis of a theoretical compound of the formula given, of two samples of Paris green carefully made, and the average analysis of 494 samples bot on the open market in Pennsylvania, are given in the following table:

ANALYSES OF PARIS GREEN

	Theoretical.	Avery, Nebraska.	Holland and Reed, Massachusetts.	Kellog, average 494 samples, Penn., 1910.
As_2O_3.....	58.55	57.55	56.94	57.97
CaO.....	31.39	31.75	31.74	29.41
$(CH_3)_2(CO)_2O$	10.06	10.31	10.37	.....
H_2O.....	.....	.....	0 78	.....
.....	100.00	99.61	99.83	.....

It is noticed that while the arsenic falls about one per cent short the amount of copper oxid is slightly increased as is the acetic acid, this may be taken to mean that there is slightly more copper acetate in the compound than is shown by the symbol.

In the solution from which Paris green is made, arsenite, acetate and copper ions must be in such concentrations, and the temperatures so adjusted as to allow the formation of the copper aceto-arsenite. Too much acetic acid will throw the white arsenious oxid out of solution. The reagents must be measured with considerable care to avoid the effect of varying masses. The base and acids concernd are all weak, and the compound is easily hydrolyzed by water; hence the long digestion to allow the formation of large particles in which the ratio of mass to surface, m/s, is greater.

QUESTIONS

(To be answerd in the notebook.)

1. Name the acidic and basic ions used in making Paris green.
2. What shaped particle has the largest ratio of m/s?
3. What are the relativ advantages of Paris greens composed of large particles; of small particles; of particles of spherical shape; of broken cornered particles? (Discuss in reference to degree of hydrolysis and time of suspension.)
4. What is the objection to putting Paris green in water several days before using? Of applying on a wet day?
5. How many grams of crystallized sodium carbonate, $Na_2CO_3 \cdot 10H_2O$, could be made from 10 grams of the anhydrous salt?
6. Water hydrolyzes Paris green. State some of the possible products of hydrolysis. Which of these are soluble?
7. Write a symbol for orthoarsenious acid; metaarsenious acid. (See textbook.)
8. Write a reaction between Na_2CO_3 and As_2O_3 naming all the substances.
9. Write the symbol of acetic acid.
10. How many grams of arsenic trioxid will react with 24 grams of dry sodium carbonate?

BORDEAUX MIXTURE

I. ORDINARY BORDEAUX

The composition of the mixture produced by the formula ordinarily used, 4–4–50, is said to be a basic sulfate of copper and lime; its composition being represented by the symbol, $CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO$.

Procedure. — Weigh out 8 grams of copper sulfate, dissolv it in 50 cc. of water, using heat if it is desired to hasten the solution, and add 350 cc. of cold water making the total volum 400 cc. Slake 8 grams of quicklime with a little water, dilute the paste with about 200 cc. of cold water and strain the mass thru a piece of cheesecloth placed over a funnel or a thistle tube. Dilute the milk of lime to 400 cc. Mix the cold solutions.

II. WOBURN BORDEAUX

Woburn Bordeaux may consist of either of three basic sulfates of copper, the proportions of base to acid in each being shown in the following formulas: $CuSO_4 \cdot 3CuO$; or $CuSO_4 \cdot 4CuO$; or $CuSO_4 \cdot 9CuO \cdot CaSO_4$. Its most striking characteristic is the absence of any free lime. Either of the three com-

pounds may be made in this experiment according to the amount of lime-water used.

Procedure. — Weigh out 0.5 gram of copper sulfate or get a solution containing that amount and dilute it to 380 cc. Measure out either 70, 74 or 84 cc. of lime-water and dilute it to 380 cc. Mix the two solutions.

Properties of Bordeaux Mixtures; Notebook.

1. Compare the color of the two mixtures.
2. Stir them up and allow to stand. Which stays in suspension best?
3. How much does each mixture settle in 15 minutes? Is a white scum to be seen on either preparation? If so which one?
4. Filter some of the Woburn Bordeaux and add a few drops of potassium ferrocyanide solution to test tube of the clear filtrate. If copper is in solution as positiv ion, in amounts of over 0.002 per cent, the brownish color of copper ferrocyanid should be seen. It may be necessary to look down the colum onto a white background to see the color and it may be well to compare this tube with another containing only water and the same number of drops of ferrocyanid solution. Are any copper ions (Cu^{++}) in solution?

NOTES

The ordinary, or one per cent, Bordeaux is made from 4 pounds of copper sulfate, 4 pounds of quicklime and 50 gallons of water. This formula is here reproduced

on a small scale suitable for laboratory purposes. The Woburn Bordeaux, if enlarged to barrel proportions, would consist of $4\frac{1}{2}$ ounces of copper sulfate, $4\frac{1}{2}$ gallons of lime-water in 51 gallons of the mixture.

Several compounds of copper can be made by mixing lime and copper sulfate in different amounts. The following symbols* show the proportions present in the various substances that can be formd:

(I) $CuSO_4 \cdot 3CuO$. (II) $CuSO_4 \cdot 4CuO$. (III) $CuSO_4 \cdot 9CuO \cdot CaSO_4$. (IV) $CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO$. (V) $CuO \cdot 3CaO$.

It will be noted that the compound (II) is more basic than (I) and that the basicity increases progressively so that (V) is all base. The compounds are produced successively, by using increased quantities of lime-water with the same amount of copper sulfate. For example, with 0.5 gram of copper sulfate, 70 cc. of lime-water will produce the compound $CuSO_4 \cdot 3CuO$, 74.1 cc. of lime-water will give $CuSO_4 \cdot 4CuO$ and 83.3 cc. of lime-water will make $CuSO_4 \cdot 9CuO \cdot CaSO_4$. Woburn Bordeaux may be any one of these

* Taken from the 11th Annual Report (p. 25) of the Woburn Experimental Fruit Farm by the Duke of Bedford and Mr. Pickering. Some calcium sulfate is reported united with the first three compounds in addition to that represented.

compounds or mixtures of them. With a large excess of the base the compound (IV) is produced having the formula $CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO$. This is still more basic in that it contains some of the basic calcium sulfate in addition to the basic copper sulfate. Such a compound the ordinary Bordeaux mixture is said to be.

From the symbol of the copper compound in ordinary Bordeaux, $CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO$, an equation may be written to account for the formation of such a substance,

$$10CuSO_4 + 12CaO_2H_2 = CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO + 8CaSO_4 + 12H_2O.$$

From this it is seen that considerable calcium sulfate is formd at the time the Bordeaux is made. Calcium sulfate is soluble in water at 25°, to the amount of 0.21 gram per liter. If any free lime is left over, which is always the case, the solubility is lessend, as both compounds contain a common calcium ion.

A rough calculation on the part of the student will show that 8 grams of copper sulfate require about 2 grams of lime to react with it. For example, the formula for the precipitate in ordinary Bordeaux is given as $CuSO_4 \cdot 9CuO \cdot CaSO_4 \cdot 3CaO$. Lime is used to produce the 9CuO and the 3CaO

making 12CaO used for every 10Cu; or more in detail, $9CaO_2H_2$ were necessary to react with $9CuSO_4$ before the resulting $9CuO_2H_2$ could form 9CuO and 3CaO are found in the product making a total of 12CaO required. The 10Cu come from $10CuSO_4 \cdot 5H_2O$ and thus the ratio between copper sulfate and lime, $10CuSO_4 \cdot 5H_2O/12CaO$, is establisht. In figures it is 2497.3/672 or 3.7 showing that nearly four times as much lime is used as is cald for by the symbol. This ratio has been fixt by horticultural practise.

From the previous paragraf it is evident that nearly four times as much lime is used as is needed. The student will inquire as to what becomes of the remainder. The solubility of calcium hydroxid at 25° is 0.16 gram in 100 cc. of water. This amount, however, is lessend by the presence of calcium sulfate so that only a small portion of the whole amount of lime dissolvs in water. Further, not all the lime weighd out gets into the preparation, as lumps, air-slaked material and frequently lime itself may be rejected by the strainer. It is obvious that all the lime not in solution must be mixt in with the precipitate.

The white scum is calcium carbonate made up of carbon dioxid from the air and

the excess lime in solution. There must be lime enuf present to precipitate all the copper before there can be any left over to react with carbon dioxid so that the formation of a white scum is proof that no copper remains in solution and that the mixture does not contain any soluble copper that can burn foliage.

Bordeaux mixture protects plants from attacks of fungous diseases. When spread over the leaf it dissolvs very slightly and disease spores blown on by the wind are kild upon germination by the soluble copper formd.

The substances which act upon the Bordeaux to make the copper soluble, to the best of our present knowledge, are the carbon dioxid, the ammonia and the nitric acid present in the atmosphere. The carbon dioxid first combines with lime forming insoluble calcium carbonate and following this begins the conversion of the copper to basic copper carbonate which is accompanied by the liberation of copper sulfate. Basic copper carbonate is dissolvd by more carbon dioxid, by ammonia, by nitric acid, or by ammonium nitrate made from the ammonia and nitric acid. The amount of soluble copper produced by the atmospheric agencies is very small, — thousandths or ten-thou-

sandths of one per cent, — while the amount of soluble copper that a leaf can stand without burning is much larger and is in the neighborhood of 0.04 per cent.

The ordinary Bordeaux mixture — containing four times as much lime as is needed for producing the insoluble copper compounds — after being spread out on the plant does not begin the liberation of soluble copper until the carbon dioxid of the atmosphere has acted on the excess of lime present. This process requires several days. On the other hand the Woburn Bordeaux having no excess of lime is acted upon by the carbon dioxid at once and soluble copper is available in a short time.

The increased vigor of plants, particularly potatoes, which is noticed when they have been sprayd with Bordeaux mixture, is due, to the best of our knowledge, to the prevention of minor insect ravages rather than a stimulating action of the very dilute copper solution on the chlorophyl. It has been shown by Pickering that potato leaves immerst in dilute copper sulfate solution give off iron and take on copper and from this it was argued that the dilute copper solution might have an accelerating effect upon the chlorophyl action. Recent work has shown, however, that the simpler explanation of in-

sect and disease prevention is the more plausible explanation of the apparent stimulation. Iron is a constituent of chlorophyl.

The rate at which Bordeaux mixture settles is an important matter. Each of the compounds I to V has a different density, is more or less voluminous and settles at a different rate from the others. Pickering states that the volums occupied by the precipitates after standing 15 minutes vary regularly and may be represented, approximately, by these numbers, 8(I), 17(II), 86(III), 98(IV), 20(interpolated) (V). This means that (IV), ordinary Bordeaux, is the most voluminous and stays in suspension best. Butler* shows that the order of mixing and the concentration of solutions at the time of mixing have a bearing on length of time the precipitate stays in suspension and recommends making a dilute copper solution and pouring this into a strong milk of lime. The directions for this exercise allow the student to make the copper and lime solutions of equal volum and pour one into the other indiscriminately. According to Butler the methods followd in this exercise take second rank in producing desirable voluminous precipitates.

* Technical Bulletin, No. 8, New Hampshire Experiment Station; also Phytopathology, 1914.

QUESTIONS

(To be answerd in the notebook.)

5. What amounts of copper sulfate and lime-water did you use in making your Woburn Bordeaux?

6. How many times as much copper sulfate is used for ordinary Bordeaux as for the Woburn mixture? How does the ordinary Bordeaux mixture differ in composition from Woburn?

7. Give a definition for a basic salt.

8. How may one test for copper?

9. What is meant by the expression 4-4-50?

10. The symbol for the compound (I) $CuSO_4 \cdot 3CuO$ may be written $4CuO \cdot SO_3$. Rewrite (II), (III) and (IV) in a similar manner. Underscore the least basic of these compounds. Double underscore the basic part of this compound.

11. What is the use of Bordeaux mixture? How does it act?

12. Figure the amount of calcium sulfate produced when the Bordeaux is made using the ratio, $10CuSO_4 : 8CaSO_4$, in the equation given in the notes. At a volum of 800 cc. what is the maximum amount that could dissolv? How much would be left undissolvd? Is the undissolvd portion present in Bordeaux mixture?

13. How much lime is used in this experiment? How much is used in the reaction? How much dissolvs in water? What becomes of the remainder?

14. What substances are in the solid part of the Bordeaux? What substances are in solution?

15. Did you observ the formation of a thin white scum on the surface of the ordinary Bordeaux? Explain what it is and how it was formd. Write the equation showing its formation.

16. What substances cause the copper to dissolv from the Bordeaux mixture?

17. What is meant by copper in a positiv ion? Copper in a negativ ion?

18. In which ion is the copper in copper sulfate? Positiv or negativ?

19. Why is the liberation of soluble copper salt from Bordeaux delayd by the presence of lime?

20. How strong a solution of copper sulfate is necessary to kill fungous spores? To kill plants?

EMULSIONS

An emulsion contains two immiscible liquids and a third colloidal substance miscible to a greater or less degree with each of the other two substances.

I. KEROSENE EMULSION

Procedure. — Weigh 5 grams of ordinary yellow soap cut into pieces to aid solution and dissolv by the aid of heat in 40 cc. of water in beaker. When solution is complete add 80 cc. of kerosene and stir vigorously, or pour from one beaker to another, until the emulsion is complete as evinst by the disappearance of the oil. This is a stock solution wh'ch is diluted with 2–10 parts of water as required.

Notebook.

1. Dilute some of the emulsion and examin a drop under the microscope. What is seen?
2. What substance mixes, to a slight extent, with both the kerosene and the water?
3. Would the decomposition of this substance destroy the emulsion? Verify by experiment and tell how it was done.
4. How long, upon standing, before kerosene separates?

II: MISCIBLE OILS

There are preparations on the market which contain various oils with the emulsifying agent already added. These are ready to use after the addition of water.

Procedure. — Making sure that all the apparatus used is clean, get 10 cc. of a miscible oil and dilute it with 12 volums of water. If free oil appears on the surface after standing a minute clean the apparatus once more and repeat the experiment.

NOTES

Kerosene emulsion is an old remedy for insects that do not chew and consequently cannot be poisond. Such sucking insects have to be attackt thru their breathing apparatus. The aphis is an examp e. Kerosene alone will burn foliage badly. The emulsion allows the use of so little kerosene that no harm is done the foliage, there still being sufficient to destroy the insect. In pract se the happy medium is sometimes hard to reach. Kerosene emulsion is practically replaced by solutions of nicotine sulfate which are obtaind from refuse tobacco.

The miscible oils are a standard remedy for scale insects and are applied in the winter or spring before the buds start. It is more

effective than the lime-sulfur as it creeps under the bark reaching all places. One thoro application of these oils will eliminate scale from an orchard.

When the miscible oil is not properly made by the manufacturer in the first place or when the apparatus used in dilution is not clean some free oil may separate upon standing. If much of any oil appears the material is worthless for spraying as the free oil kills the twigs and small lims by penetrating the bark.

In the miscible oils the oil and the third substance, a colloid in concentrated form, have been put together and it only remains to add water to make the emulsion. Their condition is comparable to eg-yolk which consists of 30 per cent fat diffused thru colloidal protein.

Some idea of emulsions may be gaind from the following remarks.

It is possible to diffuse droplets of kerosene thru water by violent agitation. Such systems are not stable as the droplets of kerosene soon coalesce and separate. This is said to be due to the great surface tension which is a name for the tendency of small drops to get together and get the most mass under the least surface. Soap solution — a colloid — has a much less surface tension than kero-

sene and droplets of kerosene mixt with soap solution will exist separately for a long time.

There is a second reason why the kerosene will stay emulsified. The droplet is mixt with the soap colloid. The concentration of the colloid is much greater on the surface of the drop than elsewhere. Now when the droplet of kerosene and soap has reacht an equilibrium, that is, the concentration of the soap solution, inside, on the surface, and outside the droplets have come into adjustment, a coalition of two droplets of kerosene would cause a readjustment of the concentration of the solution on the surface which would require energy. Consequently the droplet once in equilibrium tends to be stable.

QUESTIONS

(To be answerd in the notebook.)

5. What three substances are necessary in an emulsion?
6. Name a colloidal substance.
7. What is the use of miscible oils?
8. Which has the greater surface tension soap solution or water?
9. Define the term surface tension.
10. Where about a droplet of liquid does a colloid, when present, tend to concentrate?

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